1,009,792

NO DRAWINGS

1,009,792

Date of Application and filing Complete Specification: Aug. 8, 1963.

No. 31300/63.

Application made in Switzerland (No. 9504) on Aug 9, 1962.

Complete Specification Published: Nov. 10, 1965.

Index at acceptance:—C4 PD1C; C2 C(2B6A2, 2B6D, 2B6E, 2B6G8, 2B6J, 2B7, 3A12A4A, 3A12B7, 3A12C5)

Int. Cl.:—C 09 b // C 07 c, d

COMPLETE SPECIFICATION

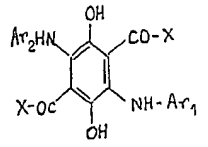
Process for the Production of Dyestuffs of the Quinacridone Quinone Series, and New Quinacridone Hydroquinone Compounds as Intermediate Products

We, J. R. GEIGY, A.G., a body corporate organised according to the laws of Switzerland, of 215 Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns a process for the production of dyestuffs of the quinacridone quinone series, and new quinacridone hydroquinone compounds as intermediate products.

Up to now, quinacridone quinone dyestuffs have been produced by reacting sulphuric acid with 2,5 - bis - (2^1 - carboxyphenylamino) - 1,4 - benzoquinone compounds. The disadvantage of this process, however, is that impure quinacridone quinone compounds are produced (R. M. Acheson and B. F. Samson, J. Chem. Soc. *1955*, 4440) which are uneconomic to purify (W. St. Lesnianski, B. *51*, 695—706 (1918)). Also, many of the suitably substiuted 2,5 - bis - (2^1 - carboxyphenylamino) - 1,4 - benzoquinone compounds which are necessary as starting materials for this process are difficult to obtain so that only a limited choice of quinacridone quinone compounds can be produced.

It has now been found that quinacridone quinone dyestuffs are obtained in a surprisingly pure form by condensing by heating a compound of formula I



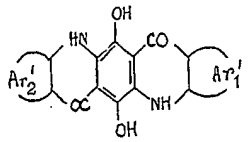
(I)

wherein

Ar_1 and Ar_2 each represent an aryl radical which contains a replaceable hydrogen atom in at least one *o*-position to the NH group and which can contain further substituents and/or fused heterocyclic rings, and

X represents an alkoxy, cycloalkoxy, aralkoxy or aryloxy group, which may be substituted

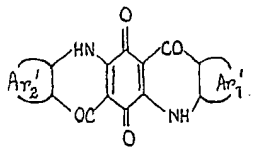
to form a compound of formula II



(II)

wherein Ar_1^1 and Ar_2^1 each complete an arylene radical corresponding to Ar_1 or Ar_2,

and oxidising this to form a compound of formula III



(III)

wherein Ar_1^1 and Ar_2^1 have the meanings given in formula II.

In formula I X represents, for example, the methoxy, ethoxy, hydroxyethoxy, propoxy, isopropoxy, n-, sec. or tert. butoxy, cyclohexyloxy, benzyloxy or phenoxy group.

Because of their easy accessibility and reactivity, those compounds of formula I are preferred in which X is a low alkoxy group which may be further substitued.

In formula I, Ar_1 and Ar_2 are, for example, of the benzene, naphthalene, pyrene or anthraquinone series; in preferred starting materials they are radicals of the benzene series. They can be identical or different; advantageously they are identical. As substituents, Ar_1 and Ar_2 can contain, for example: aliphatic groups such as the methyl, ethyl, hydroxyethyl, propyl, isopropyl, n, sec. or tert. butyl groups;

[Price

cycloaliphatic groups such as the cyclohexyl group; araliphatic groups such as the benzyl group; aromatic groups such as phenyl groups; also alkoxy, cycloalkoxy, aralkoxy or aryloxy groups which may be substituted; alkylthio, cycloalkylthio, aralkylthio or arylthio groups; halogens such as fluorine, chlorine or bromine; primary, secondary or tertiary amino groups; acylamino groups; trifluoromethyl groups, carboxylic acid ester and amide groups and sulphonic acid aryl ester and sulphonic acid amide groups (including carboxylic acid and sulphonic acid amide groups substituted at the amide nitrogen atom), acyl groups such as the acetyl or the benzoyl group; sulphonyl groups such as the methylsulphonyl, ethylsulphonyl or phenylsulphonyl group. Examples of fused heterocyclic rings are, e.g. the oxazole, thiazole or imidazole ring.

The 2,5 - bis - arylamino - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diesters of formula I usable as starting materials are obtained, for example, by reduction of the corresponding 1,4 - benzoquinone compounds with, for example, sodium hyposulphite. The 2,5 - bis - arylamino - 1,4 - benzoquinone - 3,6 - dicarboxylic acid diester compounds are produced in their turn by heating the corresponding 2,5 - bis - halogen - 1,4 - benzoquinone - 3,6 - dicarboxylic acid diesters with the amines Ar_1—NH_2 and Ar_2—NH_2, for example in a low alcohol such as in methanol or ethanol, possibly in the presence of an agent buffering acid. The 2,5 - bis - halogen - 1,4 - benzoquinone - 3,6 - dicarboxylic acid diesters are known or can be produced by methods known per se.

The ring of the compounds of formula I may be closed to form the quinacridone hydroquinones of formula II in an inert organic solvent while excluding oxidising agents at temperatures of 180 to 350°C, preferably at 220 to 260°C. Suitable solvents are principally liquids which boil above the minimal reaction temperature given, for example aromatic hydrocarbons which may be halogenated, such as diphenyl, trichlorobenzene, naphthalene, chloronaphthalenes, or aromatic carboxylic acids or their esters or anhydrides such as benzoic acid, phthalic acid diesters, e.g. phthalic acid dibutyl or dioctyl ester, or phthalic acid anhydride, heterocyclic compounds such as quinoline or diphenylene oxide and also mixtures of these solvents, e.g. the mixture of diphenyl-diphenyl oxide known under the name "Dowtherm", which is a Registered Trade Mark.

Solvents having a reducing action and particularly mixtures of solvents, e.g. alkylene and polyalkylene glycol monoethers such as ethylene glycol monophenyl ether or diethylene glycol monobutyl ether, as well as mixtures of the above solvents with hydroaromates such as tetralin, preferably in a ratio of 1:1 to 1:10 are preferred.

The quinacridone hydroquinone compounds of formula II are oxidised to form the quinone compounds of formula III for example in sulphuric acid solution, atmospheric oxygen, nitric acid or manganese dioxide being used as oxidising agents. In many cases the oxidation of the hydroquinone of formula II to the quinone compound of formula II is performed in suspension. The fine distribution of the hydroquinone which is necessary for this purpose is attained in a known manner, for example, by dissolving this compound in concentrated sulphuric acid and pouring the solution onto ice. The suspended hydroquinone of formula II can be oxidised in acid, neutral or alkaline aqueous solution as well as in organic solvents. In acid medium such as, e.g. aqueous/sulphuric acid or hydrochloric acid medium and in neutral medium water soluble salts of hexavalent chromium such as sodium or potassium chromate or bichromate, Fe(III) salts such as Fe(III) chloride or potassium ferricyanide, or tetravalent lead compounds such as lead superoxide are used as oxidising agents. In alkaline medium, for example water soluble aromatic nitro compounds such as the sodium or potassium salts of *m*-nitrobenzene sulphonic acid as well as sulphated anthraquinones, e.g. anthraquinone-1-sulphonic acid or 1,5-disulphonic acid are used as oxidising substances.

Suitable oxidising agents for an oxidation in organic solvents are, for example, halogens, particularly iodine or bromine, soluble nitrites such as sodium nitrite, or certain electrophilically substituted quinones, e.g. tetrachloroquinone. Examples of solvents used in this oxidation are glacial acetic acid or alcohols such as methanol or ethanol or ethylene glycol monomethyl or momoethyl ethers or aromatic hydrocarbons which may be halogenated, e.g. xylene, chlorobenzene or dichlorobenzene.

For economic reasons, the oxidation is preferably performed in aqueous/alkaline medium with atmospheric oxygen.

It is also possible to convert compounds of formula I in one step into the corresponding quinacridone quinones of formula III without having to isolate the hydroquinones of formula II by performing the ring closure in the presence of an oxidising agent, preferably atmospheric oxygen.

Yellow, orange, brown, red-brown and violet-brown dyestuffs are obtained by the process according to the invention which, in finely dispersed form, have remarkable colour strength and are difficultly soluble in organic solvents. They are suitable as pigment dyestuffs. As such they colour diverse organic materials such as lacquers, resins, synthetic substances etc. in the shades mentioned; the dyeings have good fastness to cross-lacquering, solvents, migration, light and heat.

The advantage of the process according to

the invention for the production of dyestuffs of the quinacridone quinone series consists in an improvement of yield and purity of the end products and is based on the fact that the starting materials used do not form any dioxazine compounds.

The following examples illustrate the invention. Where not otherwise stated, the parts are given as parts by weight. The temperatures are in degrees Centigrade. The relationship of parts by weight to parts by volume is as that of kilogrammes to litres.

EXAMPLE 1

17.5 Parts of 2,5-bis-phenylamino-1,4-hydroquinone-3,6-dicarboxylic acid diethyl ester in 200 parts by volume of chloronaphthalene are heated while stirring and introducing a weak stream of nitrogen, and the ethanol formed during the condensation is distilled off. After a temperature of over 230° has been reached, the quinacridone-6,13-hydroquinone formed begins to separate out of the reaction solution as a crystalline precipitate. The temperature is kept for 2 hours at 240—250° and then reduced to 150°. The reaction product is then filtered off, washed with ethanol and acetone and dried. 11.1 Parts of quinacridone-6,13-hydroquinone are obtained. This product dissolves in concentrated sulphuric acid with a green colour and in boiling chloronaphthalene with a violet colour; in chloronaphthalene and in organic solvents, in general it only dissolves very slightly.

For the oxidation, the quinacridone-6,13-hydroquinone is first brought into finely distributed form by dissolving it in concentrated sulphuric acid and then precipitating by pouring into water. After filtering off and washing neutral, the moist, product so obtained is suspended in 200 parts by volume of ethanol and 50 parts by volume of water, 4 parts of sodium hydroxide and 20 parts of the sodium salt of *m*-nitrobenzene sulphonic acid are added. The mixture is heated for 2 hours in a water bath during which time the oxidation to form the yellow-brown coloured quinacridone quinone occurs. This is filtered off, washed neutral with water and dried. The quinacridone-6,13-quinone so obtained dissolves in concentrated sulphuric acid with a yellow colour and, for all practical purposes, is insoluble in organic solvents. It can be used direct as pigment, for example PVC sheets being coloured in yellow-brown shades. The coloured sheets have excellent fastness to migration, heat and light.

If, instead of the 2,5-bis-phenylamino-1,4-hydroquinone-3,6-dicarboxylic acid diethyl ester, 16.3 parts of the corresponding methyl ester or 19.7 parts of the corresponding butyl ester are used and the procedure described in the example is followed, then pigments having the same properties are obtained.

The 2,5 - bis - phenylamino - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester used as starting material is produced by reaction of 2,5 - bis - phenylamino - 1,4 - benzoquinone - 3,6 - dicarboxylic acid diethyl ester, produced by condensing 2,5 - dibromo - 1,4 - benzoquinone - 3,6 - dicarboxylic acid diethyl ester with aniline in ethanol, with sodium hydrosulphite in a mixture of ethylene glycol monoethyl ether and water. This ester is orange coloured and melts at 174°. The methyl ester melts at 176° and the butyl ester at 126°. Both products are also orange coloured

EXAMPLE 2

8.8 Parts of 2,5-bis-phenylamino-1,4-hydroquinone-3,6-dicarboxylic acid diethyl ester in 100 parts by volume of diethylene glycol mono-n-butyl ether are heated at reflux temperature. After first forming a solution, the reaction mixture gradually becomes darker coloured while a crystalline precipitate is formed. After boiling for 5 hours, the reaction mixture is cooled to 100° and the precipitate is filtered off. It is washed with ethanol and dried. In this way, the quinacridone-6,13-hydroquinone described in example 1 is obtained in the form of fine, violet crystals.

The oxidation to form the quinacridone-6,13-quinone is performed in the same way as in example 1.

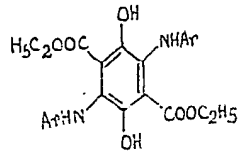
EXAMPLE 3

15.2 Parts of 2,5 - bis - (2^1 - chlorophenylamino) - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester in a mixture of 150 parts by volume of 1-chloronaphthalene and 20 parts by volume of tetrahydronaphthalene are heated to reflux temperature while stirring. The reaction product formed precipitates in crystalline form. After heating for 2 hours, this is filtered off hot, washed with ethanol and dried. In this way, 9.3 parts of 4,11-dichloroquinacridone-6,13-hydroquinone are obtained in the form of violet coloured needles which dissolve in concentrated sulphuric acid with a green-blue colour. If the product is precipitated from the sulphuric acid solution with water, then a deep violet precipitate is formed.

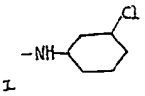
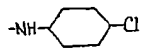
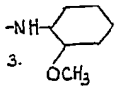
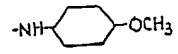
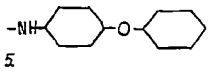
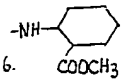
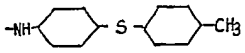
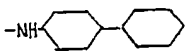
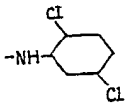
To oxidise, 5 parts of 4,11-dichloroquinacridone-6,13-hydroquinone are added to 100 parts by volume of concentrated sulphuric acid and 2 parts by volume of concentrated nitric acid are added dropwise thereto while cooling and stirring. On the addition of even the first drops of nitric acid, the colour changes from green-blue to yellow brown. The oxidised sulphuric acid solution is then poured into 500 parts by volume of water and the yellow-brown precipitate formed is filtered off and washed neutral with water. After drying, a pigment is obtained which, for example, colours lacquers or polyvinyl chloride sheets in yellow-brown shades. These dyeings have excellent fastness to cross-lacquering and migration.

If, instead of the 2,5 - bis - (2^1 - chlorophenylamino) - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester used in this

example, compounds are used of the general formula



wherein —NHAr has the meanings given in column A of the following Table I, and the procedure described in the example is followed, then pigments having similar properties are obtained. In Table I, column B shows the colour of the solution of the quinacridone hydroquinones in concentrated sulphuric acid, column C shows the colour of the solution of the quinacridone quinone pigments in concentrated sulphuric acid and column D shows the shade of polyvinyl chloride sheets dyed therewith.

No.	A	B	C	D
1.		green	yellow brown	yellow brown
2.		do	do	yellow orange
3.		do	red	brown
4.		brown-violet	orange-red	red-brown
5.		blueish-red	orange	orange
6.		blue-green	yellow	yellow
7.		green	blue	blueish red
8.		do	violet	red-brown
9.		do	red-brown	yellow-brown

The 2,5 - bis - (2^1 - chlorophenylamino) - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester used as starting material is orange coloured and melts at 156°. It is obtained by reducing the 2,5 - bis - (2^1 - chlorophenyl amino) - 1,4 - benzoquinone - 3,6 - dicarboxylic acid ester, produced by condensing 2,5-dichloro - 1,4 - benzoquinone - 3,6 - dicarboxylic acid diethyl ester with *o*-chloraniline in ethanol, in a mixture of ethylene glycol monoethyl ether and water with sodium hydrosulphite. The compounds of the above general formula, in which the —NHAr radicals have the meanings given in column A of Table I are produced in the same way also.

EXAMPLE 4

17.5 Parts of 2,5 - bis - phenylamino - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester in a mixture of 200 parts by volume of 1-chloronaphthalene and 40 parts by volume of nitrobenzene are heated to reflux temperature. As described in example 1, the quinacridone-6,13-hydroquinone precipitates in crystalline form. After boiling for 6 hours, the hydroquinone however, is completely oxidised to form the quinacridone quinone. This is filtered off at 150°, washed with ethanol and dried. 12.2 Parts of quinacridone-6,13 quinone are obtained. It dissolves in concentrated sulphuric acid with a yellow colour and can be used direct as pigment. It has the same properties as the product described in example 1.

EXAMPLE 5

14 Parts of 2,5-bis-(2^1-diphenylylamino)-1,4-hydroquinone-3,6-dicarboxylic acid diethyl ester, in a mixture consisting of 23.5 parts of diphenyl, 76.5 parts of diphenyl oxide and 20 parts by volume of tetrahydronaphthalene, are heated to reflux temperature while stirring. The quinacridone hydroquinone formed crystallises out of the deep violet coloured reaction solution. After heating for one hour, it is filtered off hot, washed with ethanol and dried. 10.7 Parts of 4,11-diphenyl-quinacridone-6,13-hydroquinone are obtained in the form of long, violet-black needles which dissolve in concentrated sulphuric acid with a green colour.

For the oxidation, the product in 200 parts by volume of *o*-dichlorobenzene is heated with 10 parts of tetrachloroquinone for 2 hours at 150—160°. The violet-black coloured hydroquinone is converted into the yellow-brown coloured 4,11 - diphenyl - quinacridone - 6,13 - quinone which is also insoluble. This is filtered off hot, washed with ethanol and dried. In this way a pigment is obtained with which, for example, stoving lacquers can be coloured in yellow-orange shades. These dyeings are excellently fast to cross-lacquering and heat.

The 2,5 - bis - (2^1 - diphenylylamino) - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester used as starting material is obtained by the method described in example 1 by reduction of the corresponding quinone. It is orange coloured and melts at 198°.

EXAMPLE 6

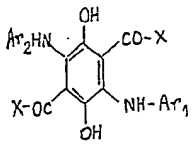
10 Parts of 2,5 - bis - (2^1 - naphthylamino)-1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester in a mixture of 100 parts by volume of 1-chloronaphthalene and 20 parts by volume of tetrahydronaphthalene are heated for 4 hours at reflux temperature. The precipitate formed is filtered off at 150° and washed with ethanol and dried. In this way, 1,2,8,9 - dibenzo - quinacridone - 16,13 - hydroquinone is obtained as a crystalline product. It dissolves in concentrated sulphuric acid, only on warming, with a red-brown colour.

For the oxidation, the product in which the ring has been closed is added to 100 parts by volume of concentrated sulphuric acid and a few drops of concentrated nitric acid are added dropwise. A yellow coloured solution is formed. This is poured into 500 parts by volume of water and the precipitate is filtered off, washed neutral with water and dried. In this way, 1,2,8,9-dibenzoquinacridone-6,13-quinone is obtained as an orange coloured pigment which, for all practical purposes, is insoluble in organic solvents.

The 2,5 - bis - (2^1 - naphthylamino) - 1,4 - hydroquinone - 3,6 - dicarboxylic acid diethyl ester used as starting material is obtained in the manner described in example 1 by reduction of the corresponding quinone. It is red coloured and melts at 183°.

WHAT WE CLAIM IS:—

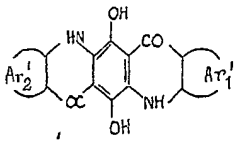
1. Process for the production of dyestuffs of the quinacridone quinone series, characterised by condensing, with heating, a compound of formula I



(I)

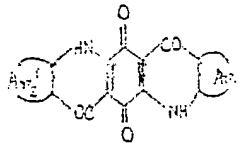
wherein Ar_1 and Ar_2 each represent an aryl radical which contains a replaceable hydrogen atom in at least one *o*-position to the —NH group and can contain substituents and/or fused heterocyclic rings, and

X represents an alkoxy, cycloalkoxy, aralkoxy or aryloxy group, which may be substituted to form a compound of formula II



(II)

wherein Ar_1^1 and Ar_2^1 each complete an arylene radical corresponding to Ar_1 and Ar_2, and oxidising this to form a compound of formula III

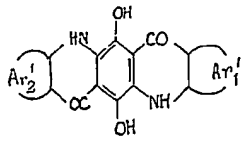


(III)

wherein Ar_1^1 and Ar_2^1 have the meanings given in formula II.

2. Process according to claim 1, characterised by the use of a compound of formula I wherein X is an alkoxy group.

3. Quinacridone hydroquinone compounds of formula II



(II)

wherein Ar_1^1 and Ar_2^1 each represent a divalent benzene or naphthalene radical which can contain substitutents.

4. A process for the manufacture of quinacridone hydroquinones of the formula II substantially as described with reference to any of the foregoing examples 1 to 6.

5. Quinacridone hydroquinones of the formula II, whenever prepared or produced by the process of manufacture hereinbefore particularly described and ascertained.

6. Quinacridone hydroquinones of the formula II as identified in the foregoing examples 1 to 6.

7. A process for the manufacture of quinacridone quinones of the formula III substantially as described with reference to any of the foregoing examples 1 to 6.

8. Quinacridone quinones of the formula III, whenever prepared or produced by the process of manufacture hereinbefore particularly described and ascertained.

9. Quinacridone quinones of the formula III as identified in the foregoing examples 1 to 6.

For the Applicants,
HENRY IMRIE & CO.,
Chartered Patent Agents,
56 Kingsway, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press, (Leamington) Ltd.—1965. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.